BIOMASS AND BIOENERGY 48 (2013) 231–238

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Effect of the carbon oxidation state of biomass compounds on the relationship between GCV and carbon content

G. Toscano*, G. Riva, E. Foppa Pedretti, D. Duca

Dipartimento di Scienze Agrarie, Alimentari ed Ambientali, Università Politecnica delle Marche, Via Brecce Bianche, 60131 Ancona (AN), Italy

ARTICLE INFO

Article history:
Received 7 April 2012
Received in revised form
25 September 2012
Accepted 5 November 2012
Available online 28 December 2012

Keywords:
Prediction model
Chemical bond
Higher heating value
Biomass elemental composition
Biofuels data

ABSTRACT

The gross calorific value of biomass is an important parameter for its applications for energy purposes. It represents the enthalpy of the complete combustion of a fuel, including the latent heat of water formed by the process. Several mathematical relationships are proposed in the literature to calculate the gross calorific value (GCV) of biomass fuels, using some characteristics as proximate analysis, ultimate analysis and chemical composition analysis. All these formulae were obtained by a mere application of statistical data elaboration, in some cases collected from literature and not from direct experimental analysis. In this study an investigation on the relationships between the chemical composition of the biomass compounds and their GCVs has been carried out. More than 650 biomass samples have been analyzed to develop four mathematical relationships between GCV and carbon content, considering the average oxidation state (C_{ox}) of the biomass compounds.

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1. Introduction

The evaluation of Gross Calorific Value (GCV) is a fundamental step in several applications of biomass for energy purposes [1–4]. The measurement of this parameter requires a specific calorimeter device and the conditions defined in EN 14918 [5] for solid biofuel and ASTM D240 for liquid biofuels [6].

Some Authors have proposed methods for determining GCV through mathematical relationships between GCV and biomass characteristics [1–4,7–12] in order to reduce the complexity, time consuming and the related costs of the laboratory determinations. Among them, elemental analysis and proximate analysis are the most important to be considered. These models are different from each other: the resulting predictions could be therefore very different and the accuracy of a correlation must be evaluated to make a proper selection [3]. The inaccuracy may be attributed to several reasons: the limited biomass samples used for its derivation, the analysis methods used in the biomass characterization and the method of deriving the formulae are the most important ones [3].

Furthermore, the GCV is a function of the energy chemical bounds in the biomass and converted into heat energy by the combustion process [2]: the variability of the biomass chemical structure determines reduction in the accuracy of the GCV prediction mathematical relationship based on element composition. This element has been investigated in the present work in order to improve the performance of the GCV prediction models. The biomass chemical composition and its relationship with the energy content have been introduced before of the description of the experimental work.

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* *Corresponding author*. Tel.: +39 071 2204297; fax: +39 071 2204167.
E-mail address: g.toscano@univpm.it (G. Toscano).

0961-9534/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biombioe.2012.11.002

2. Biomass, structures and their energy content

The term "biomass" refers to a very wide number of heterogeneous materials whose origin comes from the photosynthesis reaction, a process in which the organisms use the sunlight energy to produce carbohydrates from carbon dioxide and water. The word biomass derives from Greek (bio = life and mass = unspecified amount) and generally indicates non-fossilized organic materials originated from plants, animals and microorganisms. Biomass includes different kind of material deriving mainly from agriculture, forestry and marine fields. Their components include cellulose, hemicelluloses, lignin, extractives, lipids, fat, proteins, simple sugars, starches, water, hydrocarbons, ash and other compounds [13,14]. Their presence depends on the biomass type. For instance, proteins and lipids, typical of animal biomass, are also contained in vegetable biomass (e.g. oilseed crop) and in some microalgae [15]. Hemicelluloses, cellulose and lignin are the three main components of lignocellulosic biomass, in particular forest and agriculture materials [16,17]. The variability of the composition of these macromolecules depends on the kinds of biomass and its component (e.g. wood, branch, barks, shell, leaves, straw, pits and so on). Other minor components, like pectin, protein, extractives, resins, terpenes, gums and others may also be included [14,17,19]. In trees, cellulose is generally about 40–50% of the dry weight and the amount of lignin in wood species varies from 20% to 40%, but on average stood at 25% [15]. For lignocellulosic macromolecules literature proposes several formulae for cellulose, polysaccharide also known as glucan and glucosan and for hemicelluloses polysaccharide also known as xylan, polyose and pentosan. The ratios between the main elements are quite homogeneous, though the hemicelluloses composition, more irregular than cellulose, can vary in hardwood and softwood. The composition variability increases for the lignin components. It has been reported that lignin is a phenolic polymer whose structure can be represented by $[C_9H_{10}O_3\cdot(OCH_3)_{0.9\div1.7}]_n$. It is known that hemicelluloses is a polymer with a basic structure of $(C_5H_8O_4)_m$ and m as the degree of polymerization. The basic structure of cellulose can be denoted by $(C_6H_{10}O_5)_m$ [18,19]. The lipids have a different structure. These compound are esters derived from glycerol and fatty acids. The fatty acids composition depends on the kind of oilseed plant and structure can be generally represented by $C_nH_{(2n\pm s)}O_2$ where s is the number of insaturation. Therefore, in these compounds the carbon atoms make a number of different bonds with hydrogen and oxygen changing the energy produced by their combustion which depends on the number and type of molecule's chemical bonds [20,21]. Covalent bonds between carbon and hydrogen are energy-rich and it takes about 418 kJ to break 1 mol (6.023×10^{23}) of carbon–hydrogen (C–H) bonds [20,21].

Energy flows into the biological materials from the sun by the photosynthesis process in combination with water and carbon dioxide and produces complex organic molecules. Oxidation–reduction (red–ox) reactions are the base of this process. The energy, stored in chemical bonds of the sugars, may originate new bonds by several red–ox reactions. The reduction state of a molecule thus has a higher level of energy than in the oxidized state [21]. These different molecular conditions can be expressed by a carbon oxidation number: this is the charge that the atom would have if both the electrons in any bond are transferred to the more electronegative atoms [22]. In all organic molecules synthesized by photosynthesis process, the carbon has a lower oxidation number in comparison with the CO_2, which represents the maximum oxidation state [23]. The carbon atom reduces its oxidation number if it is linked to a less electronegative atom (as hydrogen) and increases it if linked to a more electronegative atom (as oxygen) [24]. Some theories prove the relationship between the organic molecule energy content and the carbon oxidation number [23].

The parameter that defines the energetic content of the materials is the GCV. It represents the absolute value of the specific energy of combustion for a unit of mass of solid biofuel burned in oxygen in a calorimetric bomb under the specified conditions [5]. In absence of calorimetric data, the GCV of a solid biomass may be estimated by several empirical mathematical relationships between GCV and parameters as elemental analysis, volatile matter, fixed carbon, ash content or lignin composition [1–3,7–9,11,25–27]. Some of these relationships are derived from coal [1]. Some other relationships were obtained on the base of biomass samples with a number lower than 50 [2,7–9]; often the data used to develop the models are collected by literature and not by direct experimental measurements [3,7,8,11,26]. For the latter condition, problems due to the low repeatability and reproducibility of the measurements may have affected the quality of the obtained relationships. Most of them show links of the GCV to carbon (C), hydrogen (H) and oxygen (O) contents. Some relationships concern the linkage between GCV and only the C content [4]. This kind of relationship is interesting for the central role that the carbon atom plays in organic molecules of the biomass and also in their energy content. However, the mathematical relationships proposed by literature don't take into account the aspects connected to the oxidation or reduction carbon atom state. In this work the relationship between GCV and carbon content has been analyzed considering the influence of average oxidation state of the carbon atom in the organic compounds. The study was conducted on a large number of solid and liquid biomass samples and the data were obtained only through analysis carried out in the same laboratory (Biomass Lab – D3A Department of Università Politecnica delle Marche, UNIVPM) adopting the same technical analytical standards and the same measurement systems. The work is part of a wider investigation that the UNIVPM's Biomass Lab is leading on the characteristics, properties and behavior of biomass for energy use.

3. Materials and methods

3.1. *Databases and analysis methods*

Two different databases were considered in this work: the database (DB_e) containing own data concerning measurements carried out by UNIVPM's Biomass Lab and used for developing the mathematical relationship for GCV prediction

Table 1 – Analysis and technical standards adopted on the biomass samples in the Biomass Lab.

Parameter – phase	Standard	Title	Description
Sample preparation	EN 14780 [28]	Sample preparation	Methods to reduce combined samples (or increments) to laboratory samples and laboratory samples to sub-samples and general analysis samples.
Moisture content	EN 14774-2 [29]	Solid biofuels – determination of moisture content – oven dry method – part 2: total moisture – simplified method	Method to determine the total moisture content of a sample of solid biofuels by drying it in an oven.
Ash content	EN 14775 [30]	Solid biofuels – determination of ash content	Method for the determination of the ash content of solid biofuels by thermogravimetric.
Elemental analysis	EN 15104 [31]	Solid biofuels – determination of total content of carbon, hydrogen and nitrogen – instrumental methods	A known mass of sample is burnt in oxygen under conditions to convert it into ash and gaseous products of combustion analyzed by gas analysis instruments.
Calorific value (GCV)	EN 14918 [5]	Solid biofuels – determination of calorific value	Determination of the gross calorific value of a solid biofuel at constant volume and at 25 °C reference temperature in a calorimeter calibrated by combustion of certified benzoic acid.

and the application database (DB_a) containing original data measured by the UNIVPM's Biomass Lab and other data, collected randomly from literature [1,8,26]. The DB_e contains 654 records of biomass samples of different types and origins. The samples are mainly representative of forestry and woody materials (e.g. wood chip, pellet, bark, braches, briquettes, sawdust, pruning of orchard), herbaceous (e.g. crop stalk, straws, miscanthus, arundo donax), agro-industry residues (e.g. grape marc, shells, husks, olive cake, seeds cake, stones) fats and vegetable oils. Samples of fecal and digestate products, animal wastes and special materials (e.g. pirolytic oil, torrefaction products, fatty acid methyl esters) are also included.

The physical–chemical analyses on biomass samples were carried out according to the methodologies described by CEN technical norms for solid biomass. The procedure on the biomass samples considers an initial preparation phase, in compliance with EN 14780 and then the specific analysis. Table 1 summarizes, for each parameter, the used methodologies.

The DB_a contains 240 records relevant the characteristics of different biomass and fuels, 114 of which have been measured by UNIVPM's Biomass Lab. The remaining records have been collected from the literature (113) and include also data on fossil fuels (13 records) [1].

3.2. Data processing

Several parameters have been calculated on the databases information. In particular, the atomic composition of the biomass was determined as follows:

$$C_a = \frac{C}{C_{aw}} \tag{1}$$

$$H_a = \frac{H}{H_{aw}} \tag{2}$$

$$O_a = \frac{O}{O_{aw}} \tag{3}$$

where C_{aw}, H_{aw}, O_{aw} are the atomic weights respectively of carbon, hydrogen and oxygen and C, H and O are expressed as percentage by mass as dry matter. C_a, H_a and O_a represent the number of moles of atoms each 100 g of biomass.

These data were used to determine C_{ox} defined as the carbon average oxidation number in a chemical compound. More in details, as discussed in Section 1 [24] and taking into account the chemical bonds, C_{ox} is calculated for each single record as:

$$C_{ox} = \frac{(2O_a - H_a)}{C_a} \tag{4}$$

Depending on the hydrogen, oxygen and carbon content, C_{ox} varies with molecules composition. Considering the typical atomic ratio of hemicelluloses, cellulose, lignin and triglycerides compounds and Eq. (4), three different biomass classes were determined (Table 2).

The carbon specific energy (C_{se}) was determined as ratio between GCV and C. This parameter expresses the amount of energy associated to a unit of carbon content (MJ kg^{-1} dm). For each database, descriptive statistics were applied. The mathematical relationship between GCV and C has been carried out

Table 2 – Biomass classes based on C_{ox} values.

Class	C_{ox} range	Class defined in this work	Biomass type
Low	≤ -1.0	I	Mainly tryglicerids and fatty acid or solid material with very high content of extractive lignocellulosic fraction.
Medium	> -1.0 and ≤ -0.5	II	Lignocellulosic solid material richer in lignin $C_9H_{10}O_3 \cdot (OCH_3)_{0.9-1.7}$ and containing extractives (resins, terpenes).
High	> -0.5	III	Lignocellulosic solid material richer in hemicelluloses $CH_{1.64}O_{0.78}$ and cellulose $CH_{1.67}O_{0.83}$.

Table 3 – Biomass and fuel groups included in DB_a database.

Group	Material	Data	Examples
A	Other biomass	27	Char, torrefacted material, animal wastes, bagasse, citrus residue.
D	Digestate and manure	8	Digestate, sewage sludge, poultry litter.
F	Fossil	13	Coke, methanol, antracites, C_{1-4} hydrocarbon fuel, gasoline, coal, aviation fuel.
L	Lignocellulosic	165	Herbaceous and forestal biomasses, orchard resides, husks, skins, kernel, agro-industry residues (oil extraction cake, olive residue, mar grapes, tomato residues).
O	Vegetable oil and derivates	27	Vegetable oil (sunflower, rapeseed, palm, jatropha), animal fat, methyl esters, waste cooking.

on the base of the DB_e data, using ordinary least squares regression. Three relationships between GCV and C (model H, M and L) were specifically obtained from the different groups of data based on the C_{ox} classes and further relationship (model G) on all data.

The relationships have been validated as models to be applied for predicting the GCV of the DB_a. Nine other mathematical relationships between GCV and elemental composition were selected from literature for comparison. The criteria used to evaluate the performance of the various models were based on the calculation of the mean absolute error (MAE) and mean bias error (MBE) [3].

$$MAE = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{GCV_c - GCV_m}{GCV_c}\right|\cdot 100\%$$

$$MBE = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{GCV_c - GCV_m}{GCV_c}\right]\cdot 100\%$$

where GCV_c is the gross calorific value calculated by prediction models and GCV_m the measured value.

MAE basically quantifies (on the base of the average of the set data) how close the GCV_c is to the GCV_m experimental values: a lower MAE indicates higher accuracy of a particular correlation. For MBE, a positive value indicates an overall over-estimation; a negative value indicates an overall under-estimation of the sample population. The smaller the absolute value of MBE, the smaller the bias of the correlation [3].

The evaluation of mathematical models has been performed on the overall DB_a data and also on the different group of data classified on the base of:

1. origin of the data: from UNIPM's Biomass Lab or from literature;
2. C_{ox} classes: considering that in the DB_a literature data of fossil fuels are also included, four classes are considered: fossil fuel class ($C_{ox} \le -2$); class I ($C_{ox} > -2$ and ≤ -1); class II ($C_{ox} > -1$ and ≤ -0.5); class III ($C_{ox} > -0.5$);
3. biomass classes defined as shown in Table 3.

All the statistical analysis of this work was conducted with the software MINITAB@ Release 16 using the one-way ANOVA analysis.

Table 4 – Main descriptive statistics of DB_e.

Variable	Mean	Minimum	Median	Maximum
C (%dm)	50.84	21.77	49.40	84.02
H (%dm)	6.78	3.05	6.22	13.26
O (%dm)	32.91	3.42	35.85	48.40
C_a (%dm)	4.2	1.8	4.1	7.0
H_a (%dm)	6.8	3.1	6.2	13.3
O_a (%dm)	2.1	0.2	2.2	3.0
C_{ox}	−0.56	−1.86	−0.39	0.34
GCV (MJ kg^{-1} dm)	21.349	7.323	19.558	40.444
Ash (% dm)	8.3	0.1	5.7	56.9

4. Results and discussion

4.1. *Descriptive statistics of the databases*

Descriptive statistic results of DB_e are shown in Tables 4 and 5. More in detail, Table 4 shows the mean values of each element or chemical parameter. Table 5 defines parameters for each group of biomass of the database. The values in the table show the great variability of the biomass characteristics considered in this investigation and the differences between the parameters mean values of the biomass types. C_{se} mean values show variability and are lower in the case of lingo-cellulosic, digestate and faecal materials and higher for vegetable oils and animal wastes. This parameter seems to depend on C_{ox}. In fact, C_{se} increases with C_{ox} decreasing values. If a linear regression is applied to the mean values of the parameters in Table 5, the relation $C_{se} = -74.959C_{ox} + 368.88$ is obtained, with a high regression coefficient ($R^2 = 0.9082$; p-value < 0.001).

Table 6 shows descriptive statistic results of the DB_a data. To increase the detail level, the results are also provided subdivided between experimental (UNIVPM) and literature data.

4.1.1. *Mathematical relationships*

The mean values of the main parameters of the biomass, subdivided in C_{ox} class, are shown in Table 7. It is evident that the three classes differ in terms of element composition, GCV and C_{se} mean values. The differences are greater between low C_{ox} class, mainly composed of vegetable oils and animal wastes materials and the others classes.

Table 8 shows the nine relationship selected from literature and the models L, M, H and G obtained in this work. The regression analysis has shown good results. In particular, R^2

Table 5 – Descriptive statistics of DB_e on the base of the biomass typologies.

Group of biomass	Count (n)	C (%dm)	H (%dm)	O (%dm)	C_a (%dm)	H_a (%dm)	O_a (%dm)	C_{ox}	GCV ($MJ\ kg^{-1}$ dm)	Ash (%dm)	C_{se} ($kJ\ \%^{-1}$ dm)
Arboreous	19	49.48	6.22	37.89	4.1	6.2	2.4	−0.35	19.527	4.9	395
Digestate	22	38.80	5.31	23.07	3.2	5.3	1.4	−0.74	15.958	30.4	410
Herbaceous	100	44.08	5.81	38.48	3.7	5.8	2.4	−0.26	17.604	10.6	400
Forestal	180	49.52	6.15	40.99	4.1	6.2	2.6	−0.25	19.476	2.5	394
Shells, husks and stones	24	50.49	6.33	37.40	4.2	6.3	2.3	−0.39	20.421	4.1	404
Faecal materials	40	41.66	5.21	27.19	3.5	5.2	1.7	−0.51	16.571	21.1	398
Agro-industry	108	49.91	6.28	32.40	4.2	6.3	2.0	−0.53	20.195	9.3	404
Animal wastes	12	53.23	7.99	13.34	4.4	8.0	0.8	−1.42	24.342	17.0	458
Vegetable oil and derivates	60	76.20	12.20	11.61	6.3	12.2	0.7	−1.69	39.267	0.0	516
Seeds and oil cake	89	52.31	7.22	30.63	4.4	7.2	1.9	−0.76	22.380	5.7	427

values obtained are 77.5%, 82.0%, 94.5% and 92.2% respectively for H, M, L and G model (with p-value < 0.001).

4.2. *Model validation*

The results of the statistical validation of the models applied on the DB_a are shown in Table 9. It is evident that MAE values are never lower than 5%. Best results are obtained when models are applied to UNIVPM's Biomass Lab data. Anyway, considering the MBE values, only the models M, G and 6 show an error lower than 2%. The different performances of the relationship could depend on the type of fuels in each database. UNIVPM data, as shown in Table 6, are more homogeneous in comparison to literature data. Moreover the UNIVPM data has been obtained in the same laboratory.

In Table 10 are shown the MAE and MBE values obtained by the application of the relationship to the different biomass classes. In particular, within the data of the group III several model show good results (model H, 2, 5, 6, 7, 8 and 9). Considering group II of data MAE and MBE values are higher and there are less differences between models. It is interesting to highlight as model 6, obtained from data of wood and bark samples (more rich in lignin content), shows low error when applied to the group II of data with similar characteristic (Table 2). The models H, M and L show the best results each in the group of data where they has been originated and the model G never show the best result. Finally, with the exception of the model 1 (developed on fossil fuel data), the performances of all the models are very low when applied to the fossil fuel class data.

Table 6 – Descriptive statistics of DB_a subdivided by own data (UNIVPM) or literature data.

Variable		Count	Mean	Minimum	Median	Maximum
Ash (% dm)	Total	240	6.7	0.0	3.5	71.4
	UNIVPM	126	5.7	0.0	3.4	36.7
	Literature	114	7.8	0.0	3.8	71.4
C (% dm)	Total	240	53.75	14.20	49.76	92.04
	UNIVPM	126	52.43	29.93	49.89	80.95
	Literature	114	55.21	14.20	49.45	92.04
H (% dm)	Total	240	6.70	0.43	6.13	25.15
	UNIVPM	126	6.82	3.71	6.25	13.26
	Literature	114	6.57	0.43	5.96	25.15
O (% dm)	Total	240	28.34	0.00	36.98	61.36
	UNIVPM	126	34.14	5.71	38.69	61.36
	Literature	114	21.93	0.00	24.11	47.17
GCV ($MJ\ kg^{-1}$ dm)	Total	240	22.74	4.75	19.73	55.35
	UNIVPM	126	22.00	12.67	19.56	40.40
	Literature	114	23.55	4.75	19.90	55.35

Table 7 – Average values of the main characteristics of the C_{ox} class for the DB_e data.

C_{ox} class	Range value	Count	C_{ox}	C (% dm)	H (% dm)	O (% dm)	GCV ($MJ\ kg^{-1}$ dm)	C_{se} ($kJ\ \%^{-1}$ dm)
High (H)	>-0.5	401	−0.27	47.37	5.92	38.85	18.840	398.2
Medium (M)	$>-1.0 \le -0.5$	146	−0.71	49.29	6.57	29.30	20.330	411.7
Low (L)	<-1.0	105	−1.49	66.31	10.33	15.09	32.395	481.4

Table 8 – Mathematical relationship from literature and from the regression analysis of the DB_e (GCV expresses as MJ kg^{-1} dm; C,H and O express as % dm).

Model	Mathematical relationship	Author	Notes
H	$GCV = 2.692 + 0.3409C$	Current authors	Biomass class III ($C_{ox} > -0.5$)
M	$GCV = - 2.032 + 0.4537C$	Current authors	Biomass class II ($-1.0 < C_{ox} \leq -0.5$)
L	$GCV = - 10.026 + 0.6398C$	Current authors	Biomass class I ($C_{ox} \leq -1.0$)
G	$GCV = -10.216 + 0.621C$	Current authors	All biomass ($-1.86 < C_{ox} \leq -0.34$)
1	$GCV = 0.519C + 1.625H + 0.001O^2 - 17.87$	[1]	Fossil fuels class
2	$GCV = -1.3675 + 0.3137C + 0.7009H + 0.0318O$	[2–4]	Biomass types not specified
3	$GCV = 0.4912C–0.911H + 0.1177O$	[5]	Sewages
4	$GCV = 0.971 + 0.3236C + 0.711H$	[6]	Biomass types not specified
5	$GCV = 0.2976 + 0.3897C$	[6]	Biomass types not specified
6	$GCV = 0.4373C - 1.6701$	[2–4]	Wood and bark
7	$GCV = 0.3259C + 3.4597$	[2–4]	Biomass types not specified
8	$GCV = -0.763 + 0.301C + 0.525H + 0.064O$	[2–4]	Biomass types not specified
9	$GCV = 0.320(C + 2H)$	[4]	Biomass types not specified

Table 9 – MAE and MBE values obtained from different data group.

Model	DB_a		DB_a – UNIVPM's data		DB_a – literature data	
	MAE	MBE	MAE	MBE	MAE	MBE
1	$10.21\%^{bc}$	$-6.06\%^{g}$	$7.44\%^{bcd}$	$-2.60\%^{ef}$	$13.27\%^{b}$	$-9.89\%^{e}$
2	$7.38\%^{cde}$	$-4.65\%^{fg}$	$5.81\%^{d}$	$-2.78\%^{ef}$	$9.11\%^{bc}$	$-6.72\%^{de}$
3	$19.53\%^{a}$	$9.36\%^{a}$	$18.88\%^{a}$	$11.66\%^{a}$	$20.23\%^{a}$	$6.83\%^{a}$
4	$9.47\%^{bcd}$	$4.79\%^{bc}$	$9.40\%^{bc}$	$5.77\%^{bc}$	$9.55\%^{bc}$	$3.71\%^{ab}$
5	$7.16\%^{cde}$	$-3.69\%^{fg}$	$6.20\%^{d}$	$-3.55\%^{f}$	$8.22\%^{bc}$	$-3.83\%^{cde}$
6	$6.92\%^{de}$	$-1.64\%^{def}$	$5.97\%^{d}$	$-1.46\%^{def}$	$7.97\%^{bc}$	$-1.84\%^{bcd}$
7	$8.02\%^{cde}$	$-3.88\%^{fg}$	$6.71\%^{cd}$	$-3.82\%^{f}$	$9.47\%^{bc}$	$-3.95\%^{cde}$
8	$9.06\%^{bcde}$	$-5.41\%^{fg}$	$6.87\%^{cd}$	$-2.88\%^{ef}$	$11.49\%^{bc}$	$-8.20\%^{de}$
9	$6.29\%^{e}$	$-2.92\%^{efg}$	$5.37\%^{d}$	$-2.02\%^{def}$	$7.31\%^{c}$	$-3.92\%^{cde}$
G	$8.97\%^{bcde}$	$1.63\%^{cd}$	$6.63\%^{cd}$	$1.98\%^{cd}$	$11.55\%^{bc}$	$1.22\%^{abc}$
H	$7.77\%^{cde}$	$-3.95\%^{fg}$	$6.57\%^{cd}$	$-3.87\%^{f}$	$9.11\%^{bc}$	$-4.04\%^{cde}$
M	$7.50\%^{cde}$	$0.60\%^{de}$	$6.62\%^{cd}$	$0.79\%^{de}$	$8.46\%^{bc}$	$0.39\%^{cde}$
L	$11.51\%^{b}$	$7.13\%^{ab}$	$9.88\%^{b}$	$7.52\%^{ab}$	$13.29\%^{b}$	$6.71\%^{a}$

Means followed by the same letter in columns do not differ significantly ($p \leq 0.05$).

Table 10 – MAE and MBE values obtained from different C_{ox} class group data.

Model	MAE				MBE			
	Fossil fuel class	Biomass class			Fossil fuel class	Biomass class		
		I	II	III		I	II	III
1	$7.7\%^{e}$	$17.2\%^{abc}$	$8.2\%^{abc}$	$8.5\%^{cd}$	$6.5\%^{a}$	$-10.5\%^{abcd}$	$-6.1\%^{de}$	$-5.1\%^{f}$
2	$23.8\%^{bcde}$	$14.1\%^{abc}$	$8.7\%^{abc}$	$4.2\%^{ef}$	$-23.8\%^{bcd}$	$-14.1\%^{cd}$	$-7.1\%^{e}$	$-0.1\%^{e}$
3	$54.2\%^{a}$	$17.8\%^{abc}$	$10.5\%^{ab}$	$20.9\%^{a}$	$-54.2\%^{e}$	$-17.0\%^{cd}$	$8.3\%^{ab}$	$20.9\%^{a}$
4	$16.1\%^{de}$	$11.2\%^{abc}$	$7.0\%^{bc}$	$9.3\%^{c}$	$-16.1\%^{b}$	$-2.4\%^{ab}$	$2.8\%^{bc}$	$8.5\%^{b}$
5	$34.6\%^{bc}$	$14.6\%^{abc}$	$5.8\%^{bc}$	$3.9\%^{ef}$	$-34.6\%^{cd}$	$-12.8\%^{abcd}$	$-3.0\%^{cde}$	$0.4\%^{e}$
6	$31.5\%^{bcd}$	$11.6\%^{abc}$	$5.2\%^{c}$	$4.8\%^{ef}$	$-31.5\%^{bcd}$	$-10.6\%^{abcd}$	$-0.1\%^{cd}$	$2.2\%^{cde}$
7	$37.6\%^{ab}$	$18.7\%^{ab}$	$7.3\%^{bc}$	$3.5\%^{f}$	$-37.6\%^{de}$	$-13.4\%^{bcd}$	$-4.5\%^{de}$	$0.8\%^{e}$
8	$31.4\%^{bcd}$	$19.0\%^{a}$	$10.3\%^{ab}$	$4.6\%^{ef}$	$-31.4\%^{bcd}$	$-19.0\%^{d}$	$-8.9\%^{e}$	$1.0\%^{de}$
9	$21.9\%^{bcde}$	$11.5\%^{abc}$	$6.8\%^{bc}$	$3.8\%^{ef}$	$-21.9\%^{bcd}$	$-9.6\%^{abcd}$	$-4.3\%^{de}$	$0.4\%^{e}$
G	$21.7\%^{bcde}$	$8.8\%^{bc}$	$8.7\%^{abc}$	$8.6\%^{c}$	$-21.7\%^{bcd}$	$-6.3\%^{abc}$	$6.7\%^{ab}$	$3.9\%^{cd}$
H	$37.0\%^{b}$	$17.7\%^{abc}$	$6.1\%^{bc}$	$3.5\%^{f}$	$-37.0\%^{d}$	$-13.4\%^{bcd}$	$-4.1\%^{de}$	$0.1\%^{e}$
M	$29.7\%^{bcd}$	$10.5\%^{abc}$	$5.6\%^{bc}$	$6.1\%^{de}$	$-29.7\%^{bcd}$	$-8.5\%^{abcd}$	$2.3\%^{bc}$	$4.4\%^{c}$
L	$18.1\%^{cde}$	$8.0\%^{c}$	$12.7\%^{a}$	$12.1\%^{b}$	$-18.1\%^{bc}$	$-1.3\%^{a}$	$12.2\%^{a}$	$9.7\%^{b}$

Means followed by the same letter in columns do not differ significantly ($p \leq 0.05$).

Table 11 – MAE and MBE values obtained from different biomass class of data.

Model	MAE					MBE				
	A	D	F	L	O	A	D	F	L	O
1	$14.3\%^{abc}$	$64.2\%^{a}$	$10.1\%^{b}$	$8.6\%^{bc}$	$5.5\%^{f}$	$-12.5\%^{f}$	$-62.1\%^{a}$	$-3.8\%^{ab}$	$-5.2\%^{f}$	$5.1\%^{a}$
2	$8.6\%^{cd}$	$5.4\%^{a}$	$20.1\%^{ab}$	$4.2\%^{e}$	$19.7\%^{c}$	$-6.8\%^{def}$	$-5.4\%^{a}$	$-20.1\%^{ab}$	$-0.6\%^{de}$	$-19.7\%^{fg}$
3	$20.3\%^{a}$	$3.8\%^{a}$	$32.8\%^{a}$	$17.5\%^{a}$	$27.6\%^{a}$	$16.1\%^{a}$	$0.1\%^{a}$	$-17.6\%^{ab}$	$16.6\%^{a}$	$-27.6\%^{i}$
4	$8.0\%^{cd}$	$14.8\%^{a}$	$10.7\%^{b}$	$9.0\%^{b}$	$12.4\%^{e}$	$4.7\%^{bc}$	$14.8\%^{a}$	$-10.7\%^{ab}$	$8.6\%^{b}$	$-12.4\%^{d}$
5	$6.4\%^{d}$	$10.1\%^{a}$	$19.2\%^{ab}$	$3.7\%^{e}$	$22.8\%^{b}$	$2.2\%^{bcd}$	$0.3\%^{a}$	$-16.1\%^{ab}$	$-0.8\%^{e}$	$-22.8\%^{gh}$
6	$7.9\%^{cd}$	$4.5\%^{a}$	$18.3\%^{ab}$	$4.0\%^{e}$	$18.6\%^{cd}$	$4.9\%^{bc}$	$-4.5\%^{a}$	$-12.0\%^{ab}$	$0.8\%^{cde}$	$-18.6\%^{ef}$
7	$6.4\%^{d}$	$21.9\%^{a}$	$20.8\%^{ab}$	$3.9\%^{e}$	$27.1\%^{a}$	$1.0\%^{bcde}$	$11.2\%^{a}$	$-20.1\%^{ab}$	$-0.2\%^{de}$	$-27.1\%^{i}$
8	$10.9\%^{bcd}$	$7.2\%^{a}$	$25.2\%^{ab}$	$4.9\%^{de}$	$25.0\%^{ab}$	$-8.4\%^{ef}$	$-7.2\%^{a}$	$-25.2\%^{b}$	$0.2\%^{de}$	$-25.0\%^{hi}$
9	$6.2\%^{d}$	$7.5\%^{a}$	$16.1\%^{ab}$	$3.8\%^{e}$	$17.8\%^{cd}$	$-2.6\%^{cdef}$	$3.1\%^{a}$	$-16.1\%^{ab}$	$0.3\%^{de}$	$-17.8\%^{ef}$
G	$15.2\%^{abc}$	$31.1\%^{a}$	$21.2\%^{ab}$	$6.8\%^{cd}$	$5.0\%^{f}$	10.9^{ab}	$-31.1\%^{a}$	$11.7\%^{a}$	$2.0\%^{cd}$	$4.8\%^{c}$
H	$6.3\%^{d}$	$19.0\%^{a}$	$20.4\%^{ab}$	$3.7\%^{e}$	$26.1\%^{a}$	$1.2\%^{bcde}$	$8.5\%^{a}$	$-19.3\%^{ab}$	$-0.4\%^{de}$	$-26.1\%^{i}$
M	$9.5\%^{cd}$	$3.7\%^{a}$	$18.3\%^{ab}$	$5.0\%^{de}$	$16.3\%^{d}$	$7.4\%^{abc}$	$-3.5\%^{a}$	$-9.6\%^{ab}$	$3.0\%^{c}$	$-16.3\%^{e}$
L	$18.3\%^{ab}$	$29.7\%^{a}$	$22.5\%^{ab}$	$10.3\%^{b}$	$2.7\%^{f}$	$16.7\%^{a}$	$-24.8\%^{a}$	$5.7\%^{a}$	$7.7\%^{b}$	$-0.6\%^{b}$

Means followed by the same letter in columns do not differ significantly ($p \leq 0.05$).

The performances of the models vary also when applied to the different biomass classes (Table 11). In particular, the errors are very low when the application concern lignocellulosic biomass class (L). The model 2, 5, 6, 7, 9 and H show the best performances. Regarding the biomass of the O class, the model L shows the lowest MAE value (2.7%) and very low MBE (0.6%). High error values have been shown in the case of fossil fuels class (F) where model 1 shows acceptable performance (also for L and O classes). Finally, model 3 (developed on digestate data) has good performance in D class.

5. Conclusions

This study shows that it is possible to decrease the GCV prevision errors, generally depending on the elemental composition of the fuel, by selecting a model specific for its biomass of origin. The oxidation state of the carbon atoms C_{ox} in the biofuel compounds depends on the chemical bonds between carbon with hydrogen and oxygen. C_{ox} influences the "energy weight" of a carbon unit C_{se} (Tables 5–7) affecting the performance of the relationships between GCV and the elements of its composition and, in particular, between GCV and C. The models improve their performance when applied to biomass classes in which the oxidation state of C_{ox} is similar to that of the biomass classes used to develop the models themselves. MAE values reduce more than 50% when the relationships studied in this research have been applied to data of group III (Table 10) in comparison to the MAE values obtained with all the data (DB_a – Table 9). For instance, in the case of model H, MAE values vary from 7.77% in DB_a to 3.5% in group III. For the same model, the MBE values vary from −3.95% to −0.1%. The same aspects are also evident when the relationships are applied to a different group of biomass classes data (Table 11). Examples are the model L and 3, obtained when the relationships were applied respectively to data of O and D biomass classes. In general, in order to improve the prevision of the GCV, the selection of the model would take into account the type of data from which the model was developed and also the class of data to which the model is applied.

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